Stochastic resonance in surface catalytic oxidation of carbon monoxide induced by colored noise

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Abstract The dynamical behavior of surface catalytic oxidation reaction of Pt(110)/CO+O_2 modulated by colored noise, under the condition of specific temperature, has been investigated when the partial pressure of CO gas is near the supercritical Hopf bifurcation point. By computer simulation the oscillation and stochastic resonance induced by colored noise are observed. The influences of the intensity and correlation time of colored noise on stochastic resonance are discussed. The range of sensitivity of the system to the environmental fluctuation is analyzed.

Keywords: colored noise, stochastic resonance, surface catalytic reaction of Pt(110)/CO+O_2, supercritical Hopf bifurcation, signal-to-noise ratio (SNR).

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Noise is generally considered as a disadvantageous factor, which would smear weak signals, therefore, people always try to reduce its influence. However, recent studies show that, for a nonlinear system, under certain circumstances, noise can enhance system's response to a signal. At specific noise intensity, the response of a system to a weak signal may reach its maximum, which is called "stochastic resonance" (SR). The concept of SR was originally put forward by Benzi and his collaborators[1] to account for periodically recurrent ice-ages. In recent years, many scientists have studied stochastic resonance in variety of scientific fields, and found that noise can play positive roles by SR[2]. The concept of SR has been widely extended. For example, the nonlinear system can be monostable[3,4], excitable[5—8], or thresholds-free[9—11]; external signal can be aperiodic or even chaotic[12—14], or periodic signal-free[15]; the noise can be colored, etc.

Recently people have achieved many results about the oscillation and SR induced by noise in chemical systems[16—26], of which some works have been paid to the SR without input signal. This kind of phenomenon is called "internal signal stochastic resonance" (ISSR). But white noise has been used in almost all these works to describe the influence of environmental fluctuation on the system. As a matter of fact, white noise, a too simple model, is simply an approximation which suggests that there is no correlation between them. Real white noise does not exist, because it needs infinite power to be produced. Random forces always have correlation time, therefore, it is better to use colored noise with non-zero correlation time to describe actual fluctuation. Since observed in biological system, colored noise has been extensively adopted to study biological and physical systems. However, very few works have been contributed to colored noise-induced oscillation and SR in chemical system[24—26].

The system of surface catalytic oxidation of carbon monoxide has been an important subject, because it can exhibit a lot of complex nonlinear phenomena. There have been many experimental and theoretical achievements on it[27—32]. Krischer and his coworkers[33] developed a mathematical three-variable model and conducted profound analysis and numerical simulation on it. In terms of ISSR, it is shown that the model can exhibit ISSR phenomena under the interactions of both external signal and white noise[16], and phenomena of internal signal bi-SR without input of external signals[19]. However, the influence of colored noise on the system has not yet been reported.

In the present paper, we adopt the model and modulate the partial pressure P_u of CO gas by using colored noise as the model is near the Hopf bifurcation (HB) point. By computer simulation, the colored noise-induced oscillation and ISSR are observed, and different influences of noise intensity and correlation time on the ISSR are analyzed. Meanwhile, the sensitivity of the reaction oscillation of the system to the environmental fluctuation is primarily discussed.

1 Model description

1.1 Reaction model

Following the Langmuir-Hinshelwood (LH) mechanism, the steps of catalytic oxidation reaction of CO on Pt single crystal surface are as follows:

$$\mathrm{CO\ (gas)} + * \underset{k_2}{\overset{k_u}{\rightleftharpoons}} \mathrm{CO\ (ad)} \qquad \text{(R1)}$$

$$\mathrm{O_2\ (gas)} + 2* \xrightarrow{k_v} \mathrm{2O\ (ad)} \qquad \text{(R2)}$$

$$\mathrm{CO\ (ad)} + \mathrm{O\ (ad)} \xrightarrow{k_3} \mathrm{CO_2}\uparrow + 2* \qquad \text{(R3)}$$

Krischer et al.[33] developed three-variable reaction-rate equations comprising adsorption, desorption and chemical reaction:

$$\dot{u} = k_u P_u S_u \left[1 - \left(\frac{u}{u_s}\right)^3\right] - k_2 u - k_3 uv, \qquad (1)$$

$$\dot{v} = k_v P_v S_v \left[1 - \frac{u}{u_s} - \frac{v}{v_s}\right]^2 - k_3 uv, \qquad (2)$$

$$\dot{w} = \begin{cases} -k_5 w & u \leqslant 0.2, \\ k_5 \left(\sum_{i=0}^{3} r_i u^i - w\right) & 0.2 < u < 0.5, \\ k_5 (1-w) & u \geqslant 0.5, \end{cases} \qquad (3)$$

where u, v and w stands for the coverage of CO, O and 1 × 1 phase, respectively; u_s and u_s is the saturation coverage of CO and O, respectively; k_u and k_v are their adsorption coefficients; k_2, k_3 and k_5, associated with temperature, is the desorption coefficient of CO, the reaction constant of CO with O and the phase transition coefficient, respectively, observing Arrhenius Law. S_u and S_v are sticking coefficients, here we take $S_u = 1$ and $S_v = s_{v1} w + s_{v2}(1-w)$, where s_{v1} and s_{v2} is the sticking coefficient of O_2 on the phase of 1 × 1 and 2 × 2, respectively. P_u and P_v denotes the partial pressure of CO and O_2, respectively. All the above values of parameters are taken from ref. [33] and listed in table 1.

Table 1 Parameters used in the model

Parameters	Values
Adsorptions	$k_u = 3.135\times10^3\ \mathrm{s^{-1}\cdot Pa^{-1}}$
	$k_v = 5.858\times10^3\ \mathrm{s^{-1}\cdot Pa^{-1}}$
Desorption	$k_2^0 = 2\times10^{16}\ \mathrm{s^{-1}}$, $E_2 = 159.1\ \mathrm{kJ\cdot mol^{-1}}$
Sticking coefficients	CO：$S_u = 1$
	O_2：$s_{v1} = 0.6$; $s_{v2} = 0.4$
Saturation coverage	$u_s = 1$, $v_s = 0.8$
Partial pressures	$P_{u0} = 4.08\times10^{-3}$ Pa
	$P_v = 1.3\times10^{-2}$ Pa
Reaction rate	$k_3^0 = 3\times10^6\ \mathrm{s^{-1}}$, $E_3 = 41.87\ \mathrm{kJ\cdot mol^{-1}}$
Phase transition rate	$k_5^0 = 100\ \mathrm{s^{-1}}$, $E_5 = 29.31\ \mathrm{kJ\cdot mol^{-1}}$
Phase transition coefficients	$r_3 = -1/0.0135$, $r_2 = -1.05r_3$,
	$r_1 = 0.3r_3$, $r_0 = -0.026r_3$
Temperature	$T = 539$ K

$k_i = k_i^0 \exp(-E_i / RT)$.

1.2 Random modulation of P_u by colored noise

Since the reaction temperature and partial pressure of gas are apt to be affected by environmental fluctuation, they can be used as the modulation pa-

rameters disturbed by noise. Here we take the partial pressure P_u of CO as the modulated parameter. Colored noise $\xi(\tau)$ is introduced as follows:

$$\mathrm{d}\xi(\tau)/\mathrm{d}\tau = -\xi(\tau)/\tau_0 + \Gamma(\tau), \tag{4}$$

where $\Gamma(\tau)$ is Gaussian distributed white noise with zero mean $\langle \Gamma(\tau)\rangle = 0$ and autocorrelation function $\langle \Gamma(\tau)\,\Gamma(\tau')\rangle = 2D\delta(\tau-\tau')$; $2D$ is variance (taken as 1 below for simplicity).

The mean value of the colored noise $\xi(\tau)$ is

$$\langle \xi(\tau)\rangle = \langle \xi(0)\rangle \exp(-t/\tau_0), \tag{5}$$

and the autocorrelation function of it is

$$\langle \xi(\tau)\xi(\tau')\rangle = \frac{D}{\tau_0}\exp(-|\tau-\tau'|/\tau_0) \quad (\tau/\tau_0, \tau'/\tau_0 \gg 1), \tag{6}$$

where $\langle \xi(0)\rangle$ is statistical mean value of random variable at initial time. Therefore, $\xi(\tau)$ is the exponential Gaussian colored noise, and τ_0 is the correlation time of it. Its power spectra have Lorentzian distribution form:

$$S(\omega) = \int \mathrm{e}^{-i\omega\tau}\,\frac{D}{\tau_0}\,\mathrm{e}^{-\frac{|\tau|}{\tau_0}}\,\mathrm{d}\tau = \frac{2D}{1+\omega^2{\tau_0}^2}. \tag{7}$$

By modulation

$$P_u = P_{u0}[1+\lambda\xi(\tau)] \quad (\lambda \text{ noise intensity}) \tag{8}$$

and substitution of eqs. (4) and (8) into eqs. (1)—(3), and by enlarging the dimensions of (1)—(3), we can investigate the effects of colored noise on the dynamics of this system. The constant component is chosen in such a way that the system remains in the steady state without the modulation of noise.

We separately choose three correlation time τ_0 = 0.001, 0.005, 0.009 (dimensionless) and three noise intensities λ = 0.5, 5.0, 15 (dimensionless) to study this system. By using the explicit Euler method, eqs. (1)—(3) are integrated numerically ($\mathrm{d}\tau$ = 0.001 s, total time 6500 s with transient time 4000 s omitted , total number of data 11900). To quantify the ISSR effect, the time series of u (corresponding to the coverage of CO) are analyzed by the Fourier power spectra. The value of SNR is used to measure the occurrence of ISSR (here for simplicity, SNR is defined as the ratio of the height of an output signal to that of noise background in a power spectrum).

2 Results

2.1 Stochastic resonance induced by colored noise

When λ = 0 and T = 539 K, by stability analysis and numerical computation, it is derived that at $P_u \cong 4.088\times10^{-3}$ Pa the systems (1)—(3) perform supercritical HB and enter into the oscillation region[33]. Deterministic oscillations exist within a range of $P_u \cong 4.088\times10^{-3}$—$4.235\times10^{-3}$ Pa. Fig. 1 shows the part of the variations of amplitude and frequency in the deterministic oscillation region. We can see that with the increment of P_u the frequency gradually decreases, falling to 0.0294 at $P_u = 4.22\times10^{-3}$ Pa; at $P_u = 4.1002\times10^{-3}$ Pa, the oscillation amplitude changes from small to large, meaning that the variation of coverage becomes larger. We choose $P_{u0} = 4.08\times10^{-3}$ Pa such that the system is near the HB point but remains in the steady state. We take correlation time τ_0 = 0.001, the responses of the system to four different intensities of colored noise are shown in fig. 2. When λ = 0, no response appears (fig. 2(a)); when noise intensity increases to λ = 3.2, the irregular oscillation of small amplitude emerges (fig. 2(b)), and a very short and narrow peak in the power spectrum appears (frequency

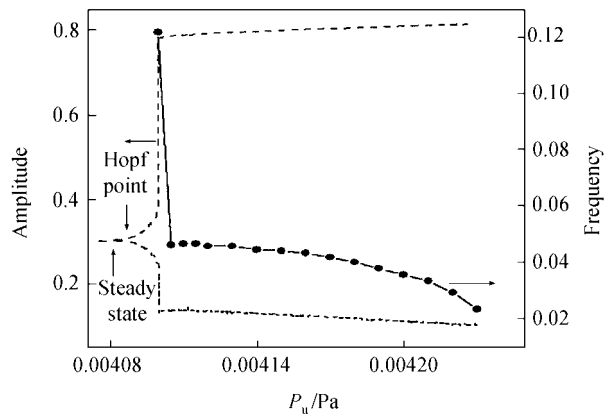

Fig. 1. Amplitude (dotted line) and frequency (solid line) of deterministic oscillation. T = 539 K, $P_v = 1.3\times10^{-2}$ Pa.

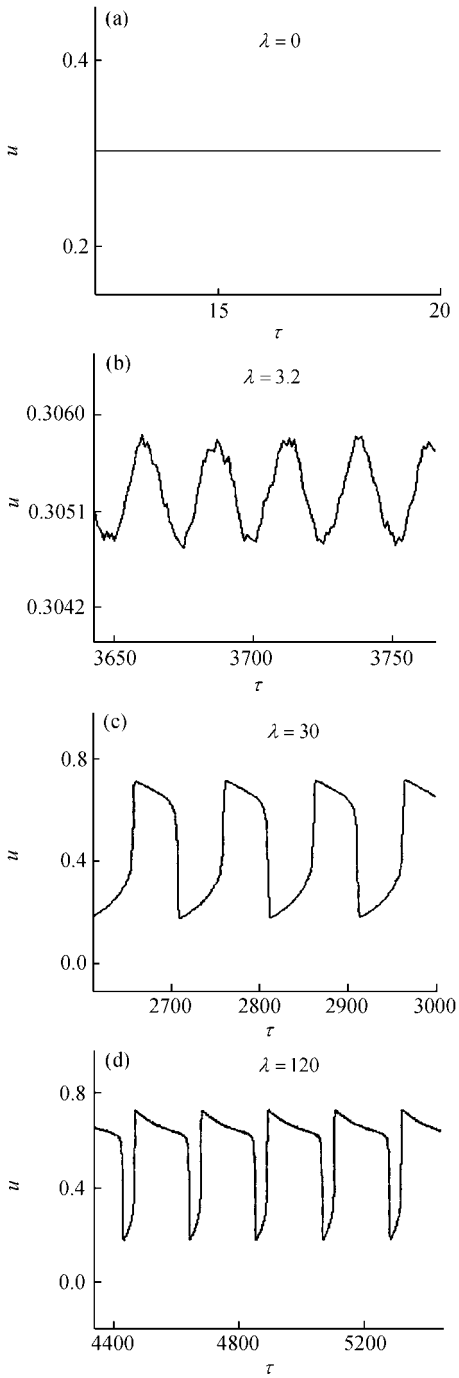

Fig. 2. Oscillation of u of the coverage of CO induced by colored noise. $\tau_0 = 0.001$, the other parameters are the same as that in fig. 1.

0.152); with the increment of noise intensity, the amplitude gradually increases, the periodicity is strengthened, and the height of peak increases, while the frequency shifts to a smaller value. At $\lambda = 9.4$, the amplitude apparently becomes large (0.176—0.72); when noise intensity continues to increase to $\lambda = 30$, the response of the system becomes quasi-periodic oscillation (fig. 2(c)), the peak reaches its largest height (frequency 0.0465) and the SNR arrives at its maximum. If the noise intensity is continually increased, however, the periodicity is weakened, the peak in the power spectrum begins to fall and to get wide (see fig. 3), meanwhile the SNR becomes small again. As the noise intensity finally increases to $\lambda = 130$, the oscillation signal is entirely flooded by noise. The above phenomenon indicates the occurrence of the ISSR.

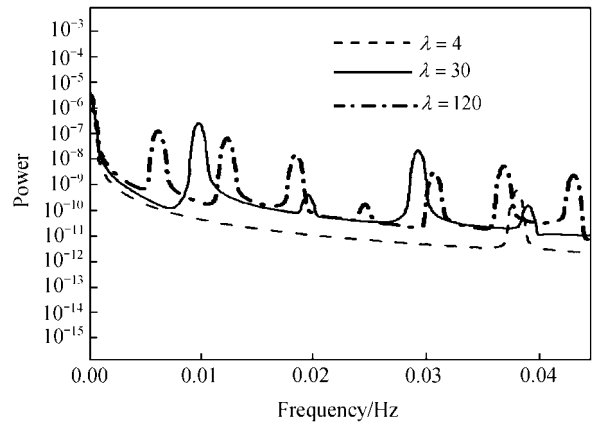

Fig. 3. Comparison of the power spectra of the oscillation induced by colored noise. $\tau_0 = 0.001$; each curve is obtained by smoothing of 20 points; the value of frequency in the figure is apparent, real value = apparent value ∶ 0.21.

2.2 Effect of colored noise with different correlation times

Given a correlation time $\tau_0 = 0.001$, with the increment of noise intensity, the SNR arrives at the maximum at $\lambda = 30$ (frequency 0.0465); but as the noise intensity is further increased, the SNR decreases; if a longer correlation time is chosen, the noise intensity for ISSR goes to smaller value correspondingly, and the maximum of SNR curve moves to the value corresponding to smaller noise intensity. For example, at $\tau_0 = 0.005$ the maximum of SNR corresponds to

λ = 8.0 (frequency 0.0458); while at τ_0 = 0.009 it corresponds to λ = 5.5 (frequency 0.045) (see fig. 4). It can be seen that the difference between the noise intensities and the maximums of the SNR curves corresponded becomes large when the correlation time increases from 0.001 to 0.005, whereas, the difference gets small when the correlation time increases from 0.005 to 0.009. This means that, although increasing correlation time can help to reduce the noise intensity for ISSR, the effect of different correlation times on the system differs greatly. It can also be seen that the noise intensity for ISSR varies when the correlation time is varied, but the basic frequency of oscillation signal for ISSR almost remains in a small range of 0.045—0.0465. From fig. 1 we know that this small range of frequency corresponds to that of the deterministic oscillation at $P_u = 4.108\times10^{-3}$—4.15×10^{-3} Pa. This indicates that, under a given specific condition, the oscillation signals of this range of frequency are apt to be strengthened by the stimulation of environmental fluctuation.

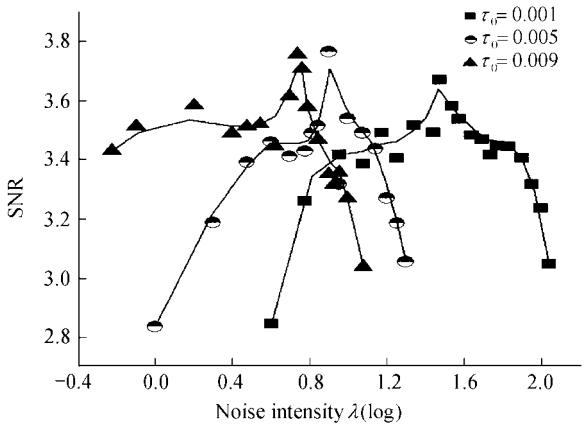

Fig. 4. The variation of SNR with colored noise intensity (solid lines denote the direction of variation).

2.3 Effects of colored noise with different noise intensities

Fig. 5 describes the variation of SNR with the increment of correlation time in the case of different colored noise intensities. Three different colored noise intensities are λ = 0.5, 5.0, 15, and the corresponding correlation time for SNR maximum is $\tau_0 \cong 0.04$, 0.004, 0.00095, respectively. The three corresponding oscillation frequencies are 0.0436, 0.0465, 0.0436. This implies that the correlation time can also induce ISSR in the system in the same way as the colored noise intensity does. It is shown from the simulation result that, when colored noise intensity gets larger, the correlation time for ISSR gets smaller, which shows that the correlation time and noise intensity of colored noise play the same role in ISSR. But it can also be seen that the correlation time decreases largely as colored noise intensity increases from λ = 5.0 to λ = 15. This makes it clear that although the correlation time for ISSR can be lessened by increasing noise intensity, the effects of different noise intensities on the system differ obviously.

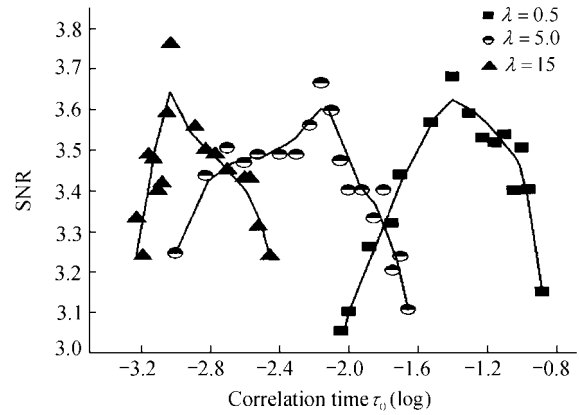

Fig. 5. Variation of SNR with correlation time (solid lines denote the direction of variation).

From the range of frequency for ISSR (0.0436—0.0465), we know by comparison of the above results that the range of the oscillation frequency for ISSR induced by correlation time is nearly in accordance with that induced by noise intensity. This makes out again that the oscillation signals of this small range of frequency are extremely sensitive to the environmental fluctuation. This theoretical result is expected to be verified in the experiment and be helpful to the experimental research.

3 Discussion

The occurrence of colored noise-induced oscillation of the system near the supercritical HB point is attributed to the random entrance of the system into

the oscillation domain under the inducement of colored noise, which consequently makes the deterministic oscillation to get randomly modulated. The larger the noise intensity, the farther the system entering into the oscillation domain. With the increment of noise intensity, the SNR curve passes by a maximum, which is namely SR phenomenon. The SR in chemical reaction can not only strengthen the weak signal and make it easier to measure it, but also bring influence on the reaction production rate and selectivity. The correlation time, an important characteristic of colored noise, has received much attention in the study on chemical reaction systems. The time correlation of exponentially correlated colored noise makes the fluctuation have the non-Markovian long-time dynamical character, which differs fundamentally in time scale from the Markovian white noise accounting for short-time dynamical behavior, consequently brings different influences on SR.

In terms of the amplitude and frequency of colored noise-induced oscillation, with the increment of colored noise intensity, the amplitude and frequency of the induced oscillation approximately consist with those of the deterministic oscillation with increasing partial pressure P_u of CO, implying that the effect of colored noise is closely associated with the inherent feature of the system. However, the ISSR simply occurs with the range of the deterministic oscillation at $P_u = 4.1082\times10^{-3}$—$4.15\times10^{-3}$ Pa, showing that the system is extremely sensitive to the environmental fluctuation.

The effect of colored noise on a nonlinear system is not only related with the character of colored noise, but also subjected to the nature of the system itself. With increasing correlation time, the colored noise intensity for SR can be not only lessened[24,26], but increased[25]. The simulation studies on the system Pt(110)/CO + O_2 show that, the larger the correlation time, namely the stronger the correlated interaction of colored noise, the smaller the noise intensity for ISSR. Thus we can say that for the present system the value of correlation time may well represent the colored noise intensity.

From the discussion in secs. 2.2 and 2.3 we can see that, the effect of different colored noise intensities or different correlation times on the system obviously differs from each other. We hence can choose the colored noise with the optimal coupling effect of both noise intensity and correlation time to modulate the chemical reaction, and expect that it will benefit more to the measurement of reaction signal and enhancement of reaction production.

It is shown by comparison of fig. 4 with fig. 5 that, the difference of the maximums of SNR is quite small, which implies that the difference of enhancements of inherent oscillation of the system by the colored noise intensity and correlation time differs not too largely.

We also find that, although the oscillation of small or large magnitude of amplitude in the present system can be induced by colored noise, the ISSR can only exist in the domain of large amplitude. This implies that the oscillation signal of large amplitude in the system has a certain selectivity for the environmental fluctuation. Study shows[19] that, for differently chosen parameters, this system with the inducement of white noise may exhibit bi-SR which separately appear in the oscillation domain of small amplitude and large one. The main reason for the above difference, besides differently chosen parameters, is undoubtedly the different characters of two kinds of noise, of which the mechanism remains to be discussed in the future.

Study has pointed out that the disturbance of a periodic force on a chemical reaction system may change the production rate and selectivity [27]. We believe that the disturbance of colored noise may bring influence on the production rate and selectivity, too.

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